



Proceedings of the Eurosensors XXIII conference

Stripping Voltammetric Measurement of Trace Metal Ions at Screen-printed Carbon and Carbon Paste Electrodes

Vernon Somerset^{a*}, Emmanuel Iwuoha^b, Lucas Hernandez^c^aNRE, Council for Scientific and Industrial Research (CSIR), PO Box 320, Stellenbosch, 7599, South Africa.^bSensorLab, Chemistry Department, University of the Western Cape, Private Bag X17, Bellville, South Africa.^cFacultad de Ciencias, Universidad Autónoma de Madrid, Campus de Cantoblanco, Cantoblanco, 28049, Madrid, Spain.

Abstract

Screen-printed carbon electrodes (SPCEs) and carbon paste electrodes (CPEs) were prepared as “mercury-free” electrochemical sensors for the determination of trace metal ions in aqueous solutions. SPCEs were coated with conducting polymer layers of either polyaniline (PANI), or polyaniline-poly(2,2'-dithiodianiline) (PANI-PDTDA). Furthermore, CPEs containing electroactive compounds with reactivity towards metal ions were employed to obtain enhanced selectivity. Optimised experimental conditions for Hg^{2+} , Pb^{2+} , Ni^{2+} and Cd^{2+} determination included the supporting electrolyte concentration, deposition potential (E_d) and accumulation time (t_{acc}). Initial results showed linearity in the examined concentration range between $1 \times 10^{-9}\text{M}$ and $1 \times 10^{-6}\text{M}$ for laboratory prepared solutions.

Keywords: SPCE; Stripping voltammetry; CPE; mercury; lead; heavy metals

1. Introduction

The analysis of heavy metal ions in environmental samples remains a challenging task since these metals ions are present at very low levels in the samples with some sample matrices being very complex in nature. The search is therefore ongoing to find new sensing materials with suitable recognition elements that can respond selectively and reversibly to specific metal ions [1]. The use of disposable sensors for the analyses of toxic metal ions has become very popular in the last two decades due to their simplicity, affordability, and ease-of-use. This has seen a growing preference for screen-printed carbon electrodes (SPCEs) that are used with stripping voltammetric techniques for metal ion determination, since they allow a high degree of sensitivity and can be mass-produced at very low costs [2,3]. Carbon paste electrodes (CPEs) under the field of chemically modified electrodes (CMEs), have received considerable attention for several years, due to its ability to accumulate metal ions on the basis of the interaction of these ions with a functional group on the electrode surface. CPEs can be easily prepared, regenerated and modified by mixing with various ligands depending on the application. They further offer a renewable and modified surface, are cheap and offer very low background current interferences [4,5]. The voltammetric determination of various trace metals after their pre-concentration at CMEs receives high interest as a research area in electroanalysis. These

* Corresponding author. Tel.: +27-21-888-2631; fax: +27-86-663-1789.

E-mail address: vsomerset@csir.co.za.

electrode surfaces are not only solid-state and mercury-free, they may exploit a chemical reaction in open circuit for the accumulation of a selected species prior to its voltammetric quantification. Several modifiers have been used in the construction of CMEs and the selection of modifier is determined by the application of the CMEs. Modifiers commonly used are organic polymers, ligands, as well as inorganic ion exchangers such as clays or zeolites [6-8]. The aim of this work was to demonstrate that SPCEs coated with conducting polymer films can be used for the stripping voltammetric determination of metal ions in electroanalysis. The use of CPEs modified with the conducting polymer of polyaniline (PANI), as well as the use of mercaptobenzothiazole (MBT), have shown that these electrode surfaces can be used for the selective pre-concentration and quantitation of Hg^{2+} , Pb^{2+} , Ni^{2+} and Cd^{2+} metal ions by differential pulse anodic stripping voltammetry.

2. Experimental

2.1. Materials and reagents

The reagents aniline (99%), N,N-dimethylformamide (98%), graphite powder (< 20 micron) and mineral oil were obtained from Aldrich, Germany. Potassium chloride, sulphuric acid (95%) and hydrochloric acid (32%) were purchased from Merck, South Africa. Mercury(II) chloride (99.5%, ACS), diethyl ether (99.8%), mercaptobenzothiazole (MBT) and ammonium persulfate (APS) were purchased from Fluka (Germany) and used as received. All other chemicals were of analytical grade, or better, and were used as received. All solutions were always prepared using Milli-Q (Millipore) water.

2.2. Apparatus

Differential pulse anodic stripping voltammetry (DPASV) was performed with the use of a conventional three-electrode cell using a BASi Epsilon Electrochemical Analyzer and Workstation. Screen-printed carbon electrodes (SPCEs) and carbon paste electrodes (CPEs) were used as the working electrodes. An Ag/AgCl electrode (saturated KCl) and a platinum wire (diam. 1 mm) were used as the reference and auxiliary electrode, respectively. All electrochemical experiments were carried out in a single compartment electrochemical cell and a room temperature of 22 ± 1 °C [2]. Scanning Electron Microscopy (SEM) measurements for morphology studies were performed using a LEO 1525 Field Emission Scanning Electron Microscope (FE-SEM) with interchangeable accelerating voltages (maximum of 15.00 kV) for optimal sensitivity. Samples were mounted on aluminium stubs using conductive glue and were then coated with a thin layer of carbon [9].

2.3. Electrode preparation

SPCEs were obtained from the Sensors and Separations Group, Department of Chemical Sciences, Dublin City University, Dublin 9, Ireland. The fabrication of the SPCE is described in the paper of Somerset *et al.*, [2]. Two sets of modified CPEs were prepared, i) polyaniline (PANI) dispersed within carbon paste and ii) mercaptobenzothiazole (MBT) dispersed within carbon paste. The modified CPEs were prepared by thoroughly homogenising PANI powder (or MBT) with graphite powder and mineral oil using an agate mortar and pestle. The paste mixtures were packed firmly into piston-driven electrode holders made of polytetrafluoroethylene cylindrical tube (i.d. 3.5 mm). The electrical contact for the carbon paste working was established with a copper rod.

2.4. Preparation of polyaniline and polyaniline-poly(2,2'-dithiodianiline) (PANI-PDTDA) polymer films

Polyaniline was prepared chemically and dried for incorporation into the modified CPE construction. Chemical synthesis of polyaniline consisted of applying equimolar (with respect to aniline) amounts of oxidizing agent, which was ammonium persulfate (APS) in this study [10]. The co-polymer film of polyaniline (PANI) and poly(2,2'-dithiodianiline) was grown electrochemically on the surface of a SPCE by repetitive cyclic voltammetric scanning at 50 mV/s from -200 to $+1100$ mV, for 10 cycles at 25 °C. Polyaniline was also electropolymerised as a monopolymer on a SPCE surface, using a 10 mL solution of 0.2 M aniline and aqueous M HCl, and cycling

repetitively at 100mV/s from -200 to $+1100$ mV for 10 cycles at $25\text{ }^{\circ}\text{C}$. Each SPCE was then rinsed with Milli-Q water and immersed in the water until use [2].

2.5. Analytical procedure

The analysis of Hg^{2+} , Pb^{2+} , Ni^{2+} and Cd^{2+} was performed using differential pulse anodic stripping voltammetry (DPASV) that was carried out in 2.0 mL aliquot samples. DPASV involved the following steps: (a) the pre-concentration step at -0.4 V for 120 s; (b) the differential pulse anodic stripping voltammograms were recorded when swept from -0.4 V to 1.5 V after 2 s quiescence. The experimental parameters used were: deposition potential, -0.4 V; accumulation time, 120 s; differential pulse amplitude (peak to peak), 50 mV; step amplitude, 4 mV; pulse width, 50 ms; pulse period, 200ms; frequency, 100 Hz.

3. Results and discussion

The results obtained for the use of differential pulse anodic stripping voltammetry (DPASV) for the evaluation of the SPCE and CPE sensors are discussed. Voltammograms for the anodic peak currents (I_{pa}) for three of the Hg^{2+} standards studied, including that of a sample blank, with the SPCE/PANI-PDTDA sensor are shown in Fig. 1. These voltammetric results indicate that a good shift in the peak current data for a small increase in the Hg^{2+} ion concentration was experienced.

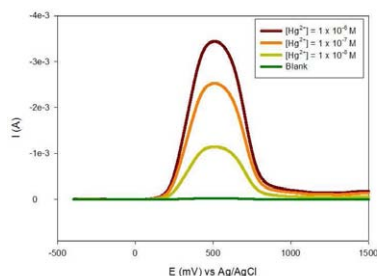


Fig. 1. Differential pulse anodic stripping voltammograms (DPASVs) obtained with the SPCE/PANI-PDTDA sensor in solutions containing Hg^{2+} concentrations of 0 M, 1×10^{-8} M, 1×10^{-7} M and 1×10^{-6} M; 0.1 M H_2SO_4 ; 0.5M HCl; $E_d = -300$ mV; $t_{acc} = 120$ s. Fig. 1. (a) first picture; (b) second picture.

Analysis of the differential pulse anodic stripping voltammograms in Fig. 1 shows that one major oxidation peak at a potential of 501.8mV (vs. Ag/AgCl) was obtained that can be attributed to Hg^{2+} ions.

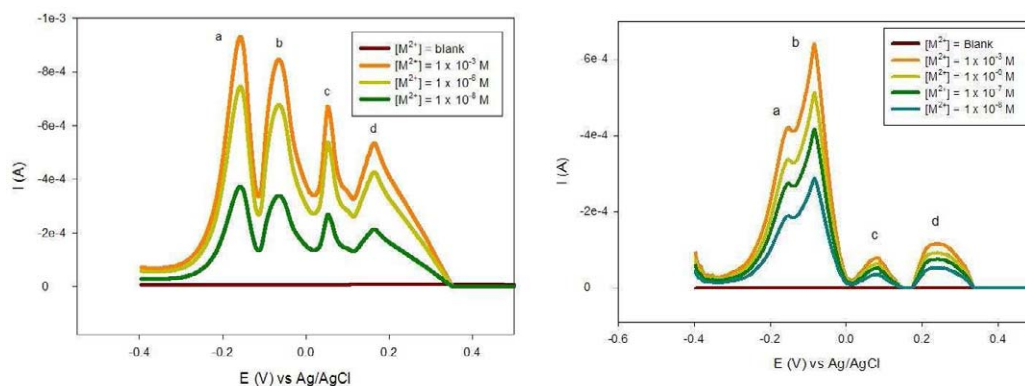


Fig. 2. on the left shows the DPASV results obtained for the stripping analysis of Cd(II), Ni(II), Pb(II) and Hg(II) using the MCPE-PANI sensor. Fig. 3. on the right shows the application of the MCPE-MBT sensor applied to the same solution containing mixed metal ions. Deposition potential, -0.4 V; accumulation time, 120 s; differential pulse amplitude (peak to peak), 50 mV; step amplitude, 4 mV; pulse width, 50 ms; pulse period, 200ms; frequency, 100 Hz.

In Fig. 2 and Fig. 3 in the diagram above, the I_{pa} data obtained for the DPASV analysis of a mixed solution containing Cd(II), Ni(II), Pb(II) and Hg(II) ions is shown. In Fig. 2 on the left, the result for the application of the MCPE-PANI is shown, while that of the MCPE-MBT sensor in Fig. 3 is on the right. The influence of various experimental parameters such as pH, accumulation potential and time in differential pulse voltammetry were studied. For the SPCE/PANI-PDTDA (Fig. 1) sensor it was found that -300 mV is an adequate accumulation, while -400 mV was appropriate for the MCPE-PANI sensor (Fig. 2) and MCPE-MBT sensor (Fig. 3). An accumulation time of 120 s was found to be adequate for the determination using the different constructed electrodes. The peak current maxima results obtained have shown that the peaks for the different metal ions can be identified as Cd(II) in a, Ni(II) in b, Pb(II) in c, and Hg(II) in d. Initial results showed linearity in the examined concentration range between 1×10^{-9} M and 1×10^{-6} M for laboratory prepared solutions, while good selectivity for the different metal ions were obtained.

4. Conclusion

A simple and effective electrode system for the single determination of Hg(II) and simultaneous determination of Cd(II), Ni(II), Pb(II) and Hg(II) was developed. Measurements of these analytes in aqueous solutions were carried out at the constructed modified electrode surfaces using DPASV. The optimized working conditions for the electroanalysis were identified and described.

Acknowledgements

This research was supported by funding received from the CSIR's parliamentary grant (PG) process, the Focus Area and RSA/Spain Bilateral Programmes of the National Research Foundation (NRF) of South Africa.

References

1. Khezri B, Amini MK, Firooz AR. An optical chemical sensor for mercury ion based on 2-mercaptopyrimidine in PVC membrane. *Anal Bioanal Chem* 2008; **390**:1943-1950.
2. Somerset V, Leaner J, Mason R, Iwuoha E, Morrin A. Development and application of a poly(2,2'-dithiodianiline) (PDTDA)-coated screen-printed carbon electrode in inorganic mercury determination, *Electrochim Acta* 2009; doi:10.1016/j.electacta.2009.01.029.
3. Yantasee W, Deibler LA, Fryxell GE, Timchalk C, Lin Y. Screen-printed electrodes modified with functionalized mesoporous silica for voltammetric analysis of toxic metal ions. *Electrochem Comm* 2005; **7**:1170-1176.
4. Mojica E-RE, Merca FE. Anodic Stripping Voltammetric Determination of Mercury (II) using Lectin-modified Carbon Paste Electrode. *Jnl Appl Sci* 2005; **5**(8): 1461-1465.
5. Raoof J-B, Ojani R, Beitollahi H. Electrocatalytic Determination of Ascorbic Acid at Chemically Modified Carbon Paste Electrode with 2,7-bis (Ferrocenyl ethynyl) Fluoren-9-one. *Intl Jnl Electrochem Sci* 2007; **2**: 534-548.
6. Arrigan DWM. Voltammetric determination of trace metals and organics after accumulation at modified electrodes. *Analyst* 1994; **119**: 1953-1966.
7. Shams E, Torabi R. Determination of nanomolar concentrations of cadmium by anodic-stripping voltammetry at a carbon paste electrode modified with zirconium phosphated amorphous silica. *Sens & Actuat B* 2006; **117**: 86-92.
8. Mousavi MF, Rahmani A, Golabi SM, Shamsipur M, Sharghi H. Differential pulse anodic stripping voltammetric determination of lead(II) with a 1,4-bis(prop-2-enyloxy)-9,10-anthraquinone modified carbon paste electrode. *Talanta* 2001; **55**: 305-312.
9. Somerset V, Leaner J, Mason R, Iwuoha E, Morrin A. Determination of inorganic mercury using a polyaniline and polyaniline-methylene blue coated screen-printed carbon electrode. *Intl Jnl Envir Anal Chem* 2009b; doi:10.1080/03067310902962536/geac.6.5.2009
10. Bhadra S, Singha NK, Khastgir D. Electrochemical Synthesis of Polyaniline and Its Comparison with Chemically Synthesized Polyaniline. *Jnl Appl Polym Sci* 2007; **104**: 1900-1904.